

Solvothermal syntheses, crystal structures and luminescent properties of two new aromatic dicarboxylate indium coordination polymers



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ABSTRACT

Two new indium coordination polymers formulated as $[\text{In}(\text{BPDA})(\text{phen})\text{Cl}]_n$ (**1**) and $[\text{In}(\text{BDC})(\text{HBDC})\cdot 2\text{DMF}]_n$ (**2**) (H_2BPDA = 2,2'-biphenyldicarboxylic acid, $\text{C}_{14}\text{H}_{10}\text{O}_4$; phen = 1,10-phenanthroline, $\text{C}_{12}\text{H}_8\text{N}_2$; H_2BDC = 1,3-benzenedicarboxylic acid, $\text{C}_8\text{H}_6\text{O}_4$; DMF = N,N-dimethylformamide, $\text{C}_3\text{H}_7\text{NO}$) have been synthesized under solvothermal conditions and characterized by single-crystal X-ray diffraction, infrared (IR), thermal gravimetric analyses (TG) and luminescent studies. Molecular structural analyses reveal that complex **1** exhibits an indium-2,2'-biphenyldicarboxylate helical chained structure decorated with 1,10-phenanthroline, and complex **2** possesses a two-dimensional (2D) layered structure constructed by 1,3-benzenedicarboxylate ligands and InO_6 octahedra, which has a (4,4) topological structure. Blue-green emission at 480 nm ($\lambda_{\text{ex}} = 340$ nm) for **1**, intense blue-green emission at 492 nm, green emission at 535 nm, and yellow-green emission at 576 nm ($\lambda_{\text{ex}} = 340$ nm) for **2** are observed in the solid state at room temperature.

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In the past few decades, the design and creation of new metal-organic functional materials with fascinating topological structures is under remarkable investigations mainly due to their potential applications in the fields of selective adsorption, separation, catalysis, and magnetism [1–4]. Since the first metal-organic complex was prepared, traditional transition metal-organic complexes have dominated the family of metal-organic materials [5–10]. With the aim to exploit new metal-organic functional solid materials, great effort has been focused on searching diverse metal centers and organic ligands. In this case, group 13 metal indium exhibits excellent prospect mainly due to two aspects: (i) The electronic structure is obviously different from those of transition metals, which can lead to novel topological structures; (ii) In^{3+} cations exhibit excellent structural and coordinative flexibility as six-coordinated MO_6 octahedra, seven-coordinated MO_7 pentagonal bi-pyramids, eight-coordinated MO_8 polyhedra, even high ten-coordinated configuration [11], which can be compared with rare-earth metals. Until now, some indium complexes with novel 0D discrete, 1D chained, 2D layered, and 3D porous structures have been successfully prepared with potential applications in adsorption, catalysis, and luminescence [12–18]. On the other hand, it's also very important to choose appropriate organic ligands, among which aromatic carboxylate ligands are usually selected for constructing metal-organic

frameworks for their strong coordination abilities and various coordination modes. In this work, we report the solvothermal syntheses, crystal structures, and luminescent properties of two new aromatic dicarboxylate indium coordination polymers, which are constructed from 2,2'-biphenyldicarboxylic acid (H_2BPDA) and 1,3-benzenedicarboxylic acid (H_2BDC) to generate the 1D helical chained structure decorated with 1,10-phenanthroline and 2D layered (4,4) topological structure for **1** and **2**, respectively.

Indium coordination polymers **1** and **2** have been successfully synthesized under solvothermal conditions. Complex **1** was synthesized from the mixture of InCl_3 , H_2BPDA , phen, and DMF [19]. Complex **2** was synthesized from the mixture of InCl_3 , H_2BDC , benzidine, and DMF [19]. During the process of syntheses, solvent and reaction time play important roles in the formation of crystals. The solubility of the reaction mixture is different in different solvents, and DMF were used in the preparation of high quality single crystals of complexes **1** and **2** instead of deionized water. Moreover, if the reaction time is too short, the single crystals of the products are usually too small; In contrast, if the reaction time is too long, powder of the products is easy to be obtained instead of single crystals. In the solvothermal syntheses of **1** and **2**, 1,10-phenanthroline and benzidine are employed as auxiliary ligands, and the single crystal structures reveal that 1,10-phenanthroline is more easy to coordinate with In^{3+} cations than benzidine molecule. Though benzidine was not incorporated in the final product of complex **2**, it plays an important role to regulate the pH value of the reaction mixtures.

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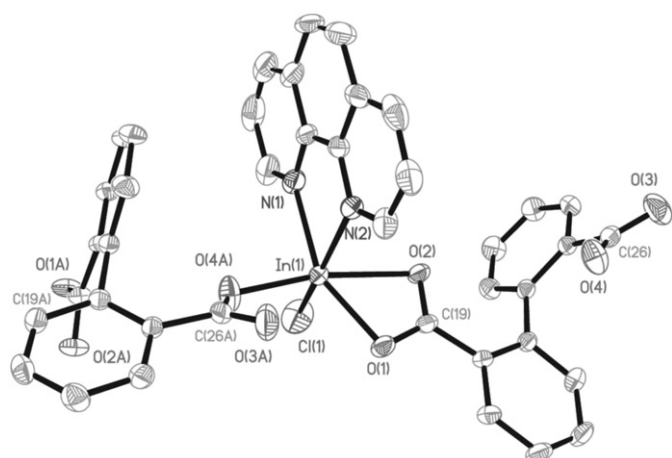


Fig. 1. A view of the environments of central In^{3+} cation in complex **1**.

The elemental analyses results reveal that the components of indium coordination polymers **1** and **2** are in agreement with their formula. The IR spectra show that the carboxyl groups of the free aromatic dicarboxylate ligands have characteristic adsorption bands at around 1700 cm^{-1} . When it coordinates with central In^{3+} ions, the absorption peak splits into two peaks (1605 and 1408 cm^{-1} for **1**; 1619 and 1405 cm^{-1} for **2**), which correspond to symmetric and asymmetric stretching vibrations of the carboxyl groups, respectively. The intensity of the absorption peaks is obviously decreased and stretching bands of the carboxyl groups shift toward lower frequencies, which reveal that the carboxyl oxygen atoms are coordinated with the In^{3+} cations.

Single crystal X-ray diffraction analysis [20] reveals that indium coordination polymer **1** crystallizes in the monoclinic space group $P2_1/n$. As shown in Fig. 1, the asymmetric unit of **1** is comprised of one crystallographically independent $\text{In}(1)^{3+}$ cation, one BPDA^{2-} anion, one Cl^- anion, and one neutral phen molecule. Each In^{3+} cation is six-coordinated by three carboxyl oxygen atoms (O(1), O(2), O(4A)) of two BPDA^{2-} anions, two nitrogen atoms (N(1), N(2)) from one phen molecule, and one Cl^- , forming a distorted $\text{InO}_3\text{N}_2\text{Cl}$ octahedron motif. In the molecular structure of **1**, the two carboxyl groups of each BPDA^{2-} ligand have two different coordination modes (Scheme 1). One carboxyl group adopts monodentate coordination mode and coordinates with the central In^{3+} cation through one carboxyl oxygen atom (O(4)), with the other carboxyl oxygen atom (O(3)) isolated. The bond distance of $\text{In}(1)-\text{O}(4)$ is $2.081(3)\text{ \AA}$. The other carboxyl group adopts bidentate chelating mode and chelates with the central In^{3+} cation through two carboxyl oxygen atoms (O(1), O(2)), with bond distances of $2.174(3)\text{ \AA}$ and $2.329(3)\text{ \AA}$ for $\text{In}(1)-\text{O}(1)$ and $\text{In}(1)-\text{O}(2)$, respectively. When bidentate chelating with the central In^{3+} , the $\text{In}-\text{O}$

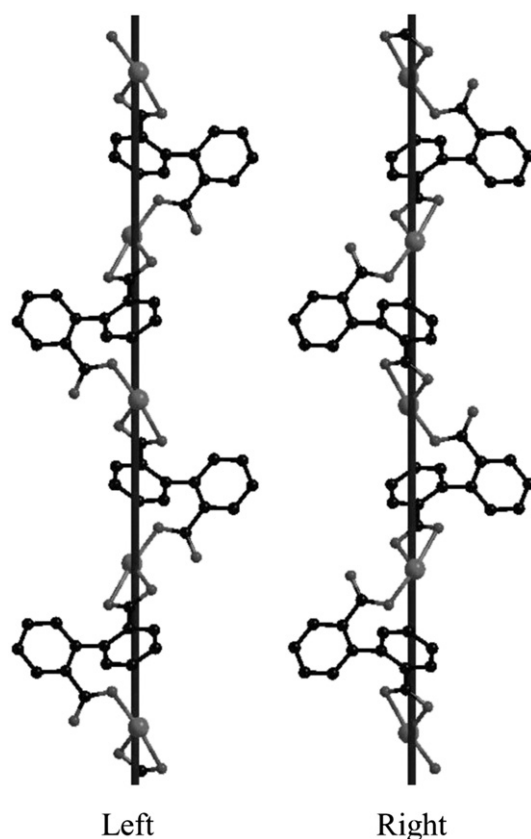
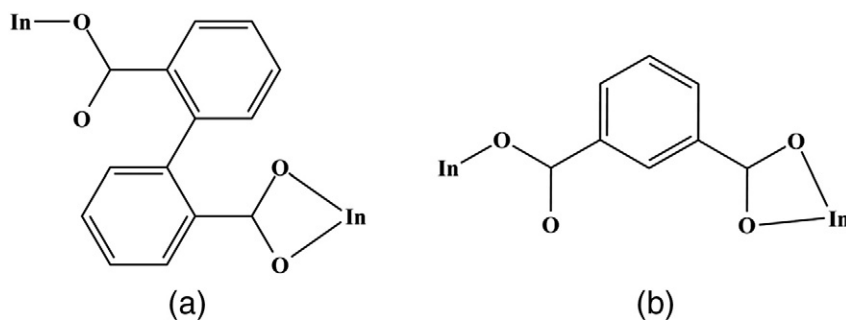


Fig. 2. Ball-and-stick views of two neighboring left- and right-handed helical chains in complex **1** (phen molecules and Cl^- anions are omitted for clarity).

bonds exhibit longer distances than those of monodentate coordination. The bond distances of $\text{In}(1)-\text{N}(1)$ and $\text{In}(1)-\text{N}(2)$ are $2.278(3)$ and $2.285(3)\text{ \AA}$, respectively. Among the bonds coordinated to the central In^{3+} cation, the $\text{In}(1)-\text{Cl}(1)$ bond distance is $2.4159(13)$, which is the longest. The bond distances of $\text{C}-\text{O}$ are varying from $1.236(5)$ to $1.277(4)\text{ \AA}$, and the uncoordinated $\text{C}(26)-\text{O}(3)$ bond is the shortest, with the bond distance $1.236(5)\text{ \AA}$. Besides, the bond angles of the carboxyl group arms will become small when chelating with the central In^{3+} , with bond angles of $118.0(3)$ and $122.3(4)^\circ$ for $\text{O}(1)-\text{C}(19)-\text{O}(2)$ and $\text{O}(3)-\text{C}(26)-\text{O}(4)$. These phenomena also exist in other reported carboxylate indium MOFs [12–18]. As shown in Fig. 2, each BPDA^{2-} anion connects two In^{3+} cations through three carboxyl oxygen atoms (O(1), O(2), O(4)) of the two carboxyl groups and every two BPDA^{2-} anions are joined by one In^{3+} cation. The BPDA^{2-} anions and In^{3+} cations join each other alternately to generate the left- and right-handed helical chains in



Scheme 1. The coordination modes of ligand $2,2'$ - BPDA^{2-} in **1** (a) and $1,3$ - BDC^{2-} in **2** (b).

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